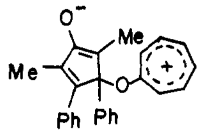

XVIII

When II or Va was heated above 100°, equilibrium between tropone, I, II, and Va was rapidly attained before formation of XI was noted, so that no information is available as to the origin of XI. However, the presence of XVII was never detected by nmr, and the direct Cope rearrangement of II to XI is sterically impossible, so that the concerted formation of XI is implied.

A second example now exists of competing *exo* [6 + 4] and *endo* [4 + 2] cycloadditions, lending further support to the Woodward–Hoffmann explanation of *exo–endo* phenomena.[2,14]

Acknowledgment. The financial support of the National Institutes of Health and the National Science Foundation (Harvard) and the donors of the Petroleum Research Fund, administered by the American Chemical Society (L. S. U.), is gratefully acknowledged.

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K. N. Houk
Department of Chemistry, Louisiana State University
Baton Rouge, Louisiana 70803

R. B. Woodward
Department of Chemistry, Harvard University
Cambridge, Massachusetts 02138

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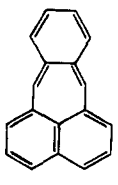
Photochemical Synthesis of Matrix-Isolated Pleiadene

Sir:

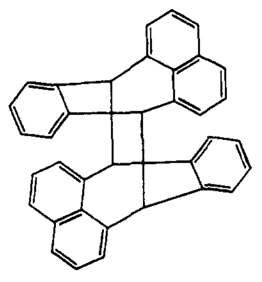
Pleiadene[1] (I) has long been a subject of theoretical[2] and experimental[3] interest but has never been directly observed. Cava and Schlessinger[3b] succeeded in generating I which could be trapped with N-phenylmaleimide but otherwise dimerized immediately to II; identical results were obtained for simple derivatives.[3c]

We wish to report a photochemical preparation and spectral characterization of stable matrix-isolated I using a novel precursor, 6b,10b-dihydrobenzo[1,2]-cyclobut[3,4-*a*]acenaphthylene (III). The unusual path followed in the photochemical process is discussed in the following communication.[4]

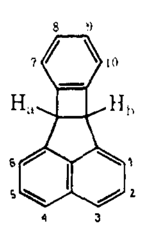
Benzyne (anthranilic acid and amyl nitrite in boiling CH_2Cl_2) adds to acenaphthylene; III was isolated in 8–10% yield by preparative thin-layer chromatography on silica gel with petroleum ether eluent: mp 133–134°, elemental analysis correct for $C_{18}H_{12}$, mass spectrum shows strong peaks at *m/e* 228 (M^+), 226 ($M^+ -$ 2H), 114 (M^{2+}), and 113 ($M^{2+} -$ 2H), and no higher peaks up to *m/e* 750. The uv absorption spectrum closely resembles a superposition of the spectra of benzocyclobutene[5] and acenaphthene.[6] Proton nmr spectra in acetone-d_6 (60, 100, 220 MHz, TMS internal standard) show an ABC system integrating for 6 H (approximately τ_1 2.45, τ_2 2.53, τ_3 2.37, J_{12} = 7 Hz, J_{23} = 8 Hz), an AA′BB′ system centered at τ 2.84 (4 H), and a broad singlet at 4.67 (2 H, half-width 1.7 Hz). Decoupling showed that the broadening is due to unresolved long-range coupling between the aliphatic protons and both aromatic systems. From measurements of ^{13}C satellites, $J_{H_aH_b}$ = 3.5 ± 0.3 Hz, $J_{^{13}CH_a}$ = 147.4 ± 0.5 Hz. These results compare well with available data for related molecules[7,8a] and leave no doubt about the structure of III.



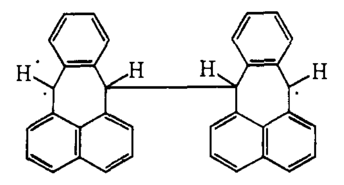
I



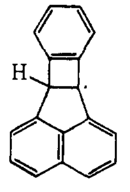
II



III



IV



V

Benzocyclobutenes open thermally and photochemically to *o*-quinodimethanes.[8] By analogy, we expected III to give I. Although III is thermally quite stable (unchanged after 6 min at 170°), at 230–240° its melt solidifies in *ca.* 5 min and gives II, identified by comparison of the decomposition point and nmr and uv spectra with Cava's values[3b] (good agreement except for a reported uv peak at 214 nm in dioxane solvent, which we believe is spurious).

Irradiation of the colorless rigid solution of III in glass-forming solvents at low temperatures with uv light produces a stable yellow-green coloration, which we assign to I. The change can be followed spectrally: bands of I grow continuously while those of III gradually disappear (several isosbestic points). The spectrum of I is virtually the same in all solvents tested. After complete disappearance of III, further irradiation with uv, visible, or near-ir light produces no change. Thorough attempts to detect an epr signal gave negative results (glycerol–methanol, 9:1, 195°K). When a

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(3) (a) L. F. Fieser, *ibid.*, **55**, 4977 (1933); (b) M. P. Cava and R. H. Schlessinger, *Tetrahedron*, **21**, 3073 (1965); (c) M. P. Cava and W. S. Lee, *ibid.*, **24**, 837 (1968); M. P. Cava, W. S. Lee, and D. F. Barringer, *ibid.*, **23**, 4557 (1967); M. P. Cava and R. H. Schlessinger, *ibid.*, **21**, 3065 (1965).

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fully converted sample is allowed to warm up until the glass starts to melt, the green color disappears in 10–15 sec (*e.g.*, in 3-methylpentane this occurs at *ca.* 110°K). Recooling at this point and recording the uv spectrum give a curve identical with that of II. Using a vacuum-line degassed solution of III (*ca.* 10^{-4} *M*), the resulting spectrum of II has about 80% of the intensity expected theoretically for 100% conversions in both steps, showing that side reactions are unimportant. In concentrated solutions a large degree of conversion is much harder to achieve, so that preparative work is difficult. However, after repeated irradiation and thawing II was isolated by thin-layer chromatography, and identified by comparison of its uv spectrum, R_f value (tlc), and decomposition point with those of the sample prepared thermally.

The rate of the reaction 2I → II is striking. It is "forbidden" as a thermal concerted process (4 + 4 cycloaddition).[9] However, it is "forbidden much less than most others," because of the undoubtedly relatively low energy of the doubly excited $1,1 \rightarrow -1,-1$ configuration in I which correlates with the ground state of II. Probably more important, this is an unusually favorable case for a nonconcerted mechanism. Using heats of formation calculated by Dewar and coworkers,[10] formation of 1 mol of the intermediate IV should be actually exothermic by *ca.* 5 kcal.

The absorption spectrum of I has two band systems in the visible region: 11,500–20,000 cm^{-1} ($\epsilon \cong 1000$) and 22,000–29,000 cm^{-1} ($\epsilon \cong 15{,}000$), both composed of progressions in *ca.* 1200 and *ca.* 1500 cm^{-1} vibrations. The uv region contains poorly resolved band systems at 30,000–34,000 cm^{-1} ($\epsilon \cong 5000$), 35,500–38,000 cm^{-1} ($\epsilon \cong 30{,}000$), 38,500–40,000 cm^{-1} ($\epsilon \cong 40{,}000$), 41,500–44,000 ($\epsilon \cong 30{,}000$), and 46,000 cm^{-1} ($\epsilon \cong 40{,}000$). These values are in good agreement with results of semiempirical SCF-PPP calculations using parameters of ref 11. The calculations also account well for the differences between the spectrum of I and that reported[12] for the closely related acepleiadylene.

When light of wavelengths above 280 nm is used in the photochemical reaction, I is the only product that can be detected by absorption spectroscopy. When shorter wavelengths are present and the irradiation is done at 77°K, I still is the main product but presence of several additional very small spectral peaks indicates formation of a by-product, possibly the radical V.[13]

Work on these and other aspects of the chemistry of I and III is being continued.

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(13) The amount of the by-product is proportional to the square of light intensity and depends on the solvent, lamp, and filter used. It is even more reactive than I: on slow warming its peaks disappear before the peaks of I are affected. Its formation may be related to the well-known radical-producing photosensitized decomposition of 3-MP and other rigid-glass solvents due to absorption of two photons by a solute *via* its metastable lowest triplet state[14,15] which proceeds only with sufficiently energetic photons (for naphthalene[15] $\lambda < 260$ nm). Compounds with a benzylic hydrogen give benzyl radicals.[16,17] Since the peaks of our by-product are not reduced by irradiation with intense near-ir or visible light (no absorption due to solvated electrons is seen in the 1500-nm region), assignment to radical cations of III or I is much less attractive although biphotonic photoionization under similar conditions is also known.[17,18]

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(19) To whom correspondence should be addressed: Department of Physics, University of Utah, Salt Lake City, Utah 84112.

J. Kolc, J. Michl[19]
Department of Chemistry, Aarhus University
8000 Aarhus C, Denmark

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A Photochemical Electrocyclic Reaction Requiring an Upper Triplet State

Sir:

We wish to present evidence that the photochemical conversion[1] I → II does not proceed from excited singlets nor the lowest triplet, but occurs from one (or several) of the upper triplet states. This is of interest for the understanding of the mechanism of photochemical electrocyclic reactions.

(a) II is known to dimerize very fast in solution at low[1] and room[2] temperatures. At room temperature, irradiation of a vacuum-line degassed solution of I (2×10^{-3} *M*) in 3-methylpentane (3-MP) with 1-kW Xe-Hg arc (Corning 9863 filter) gives no dimer of II. After 6 hr, over 90% of I is still present.[3] Irradiated

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(1) J. Kolc and J. Michl, *J. Amer. Chem. Soc.*, **92**, 4147 (1970).

(2) M. P. Cava and R. H. Schlessinger, *Tetrahedron*, **21**, 3073 (1965).

(3) After 13 hr I is absent; a solid (polymer?) has precipitated, but no dimer of II can be detected. Similar results are obtained under other experimental conditions. The eventual destruction of I proceeds faster when very energetic light is not removed (no filter). This lack of electrocyclic reactivity is to be contrasted with the smooth formation of the dimer of II in high yield when III is irradiated 1–2 hr with a 100-W Hg lamp in liquid solution with or without sensitizer[4,5] and with the facile photochemical ring opening in IV[6] and V (can be sensitized).[7]